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Combinatorial Chemistry Approach to Development of Molecular Plastic Solar Cells

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Abstract. We used a combinatorial chemistry approach to develop the molecular plastic solar cells based on soluble fullerene derivatives or solubilized TCNQ molecules in combination with conjugated polymers. Profiles, formed by the diffusion of low molecular weight component in the spin-cast polymer host were used. The ratio between low molecular weight acceptor and polymer changed along the diffusion gradient direction from 100% to 0% at the distances 10-20 mm. Optical and electrophysical properties such as absorption, luminescence, short circuit current and open circuit voltage were measured using a specially designed installation with the resolution of 25 points per millimetre.

EXPERIMENTAL

As a first step on a way to develop molecular plastic solar cells using both advanced organic synthesis and supramolecular engineering approach on the device scale level we developed the combinatorial chemistry technique to investigate the behaviour of soluble fullerenes and TCNQ derivatives when mixed with the substituted BW-poly(paraphenylenevinylene) matrix. The method is based on the diffusion profiles, produced by low-molecular weight component and spreading from the phase boundary into the polymer layer as far as 20 -30 mm. This is realised by means of putting the small drop of fullerene or TCNQ derivative, dissolved in mixture of toluene and chloroform in the centre of spin-cast BW-PPV layer. Since toluene swells the polymer, almost not dissolving it, and chloroform dissolves the polymer, varying the ratio between these two components, one can control the ratio between the diffusion through the swollen matrix and mutual intersolubility. This way we obtain the concentrations of fullerene within a polymer ranging from 100% to 0% at distances of 20-30 mm.

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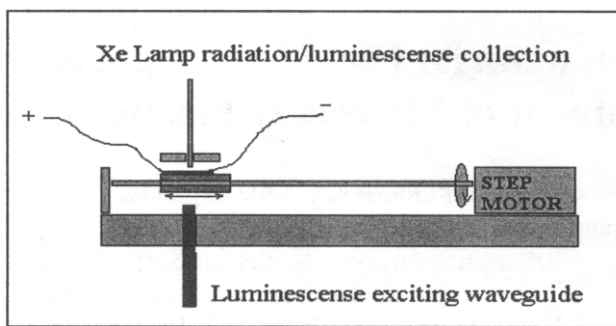


FIGURE 1. Installation Scheme.

In order to study the optical and photovoltaic properties of obtained mixtures the scanning measurement technique was developed (Fig.1), which allows to measure absorbance, photoluminescence, short circuit current and open circuit voltage with the spatial resolution as high as 25 points per millimetre. The scanning photoluminescence, short circuit current and open circuit voltage measurements are realised by means of focusing the light from Xe-lamp or luminescence exiting monochromatic light (WL ca.400 nm) onto the surface of the sample, which is then moved stepwise using the mechanical drive. The focused spot size is around 100 microns and each step moves the sample by 30 microns, thus allowing the measurements with the resolution of ca. 50 microns. The scanning absorbance measurements are realised by means of projecting of collimated beam from the Xenon lamp through the sample onto CCD array. The method permits us to make 500-1000 points measurements of all mentioned parameters depending on the ratio between soluble C_{60} or TCNQ derivatives and polymer which is changed from 0/1 to almost 1/0 along the diffusion gradient profile. The scanning absorbance and luminescence spectra of one of the fullerene derivatives blended with BW-PPV can be seen from Fig. 2. The ratio between peaks on the absorbance spectra of the blends compared with the absorbance of the ethalon blend structures, made for reference allowed us to estimate the ratio between the polymer and fullerene derivative along the diffusion profile.

RESULTS AND DISCUSSION

All the results are combined in concentration as estimated from the absorbance spectra. It can be seen, that luminescence is quenched completely within the fullerene concentration range of around 3 vol.%. This points out the fact that there is basically no problem with the photoinduced charge transfer in the molecular plastic solar cells. The more important problem is to separate charges on the device level to avoid recombination.

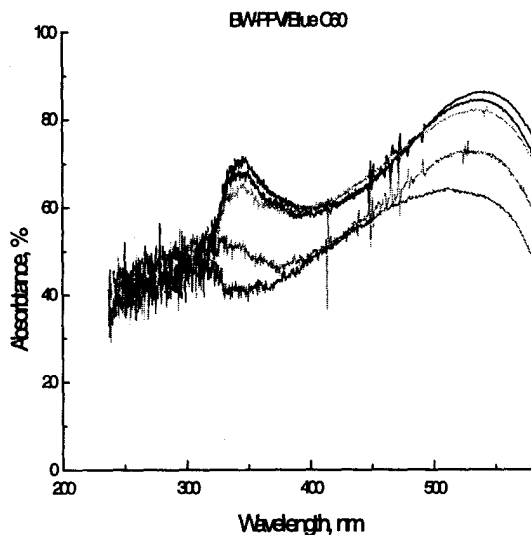


Figure 2. Scanning absorbance (distance between measurement points 300 microns) (a) and luminescence (distance between measurement points 100 microns) (b) spectra of BW-PPV+C60 blends along the diffusion profile.

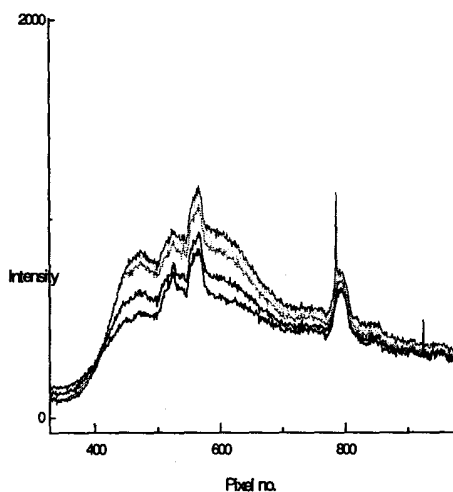


Figure 3. This figure shows the change of luminescence intensity, short circuit current and approximate fullerene derivative volume

The dependence of short circuit current on the fullerene concentration looks quite surprising, since it manifests the fact that the more fullerene we add to the blend up to the concentrations as high as ca.90 vol. % the higher short circuit current is. This fact contradicts the existing paradigm, stating that photoinduced charge transfer from polymer to fullerene is the main source of photocurrent. A probable explanation follows from the analysis of IPCE spectra of the blends (to be communicated elsewhere) which shows significant peak at 320-350 nm associated with $C_{60} h_u - t_{1g}$ which provides up to 60 % of the photocurrent once illuminated by AM01 Sun Spectral Ethalon.

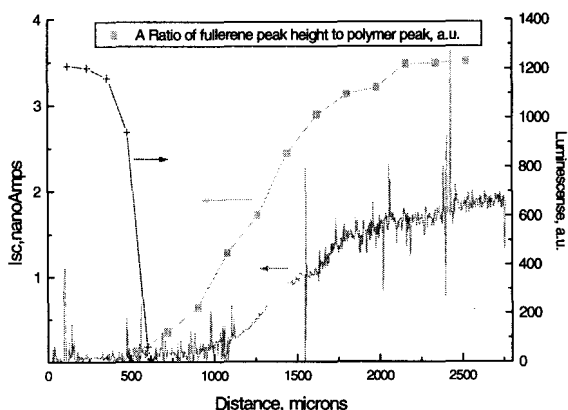


Figure 4. The dependencies of luminescence, I_{sc} and concentration on distance along diffusion gradient.

The difference between the sharp interface structures and blends is provided by the nanocrystalline character of fullerene phase in blends. If in the bulk fullerene layer the electron excited to the t_{1g} level can easily drop down to the long living h_{1g} , in the nanocrystal this process can be suppressed due to discrete character of phonon spectrum, and difficulty to dissipate the energy of the order of 1 eV. This fact probably gives rise to the enhanced quantum efficiency of $h_u - t_{1g}$ transition in polymer-fullerene blends with the phase separation on the nanometer scale.

CONCLUSIONS

The first conclusion that we would like to outline consists of the fact that the combinatorial technique along with the scanning optical and photovoltaic parameters measurements is a convenient tool for the investigation of polymer photovoltaic solar cells, since it allows to avoid the routine blend-and measure way of studying the concentration dependencies.

The second result is that the photovoltaic properties of fullerene based photovoltaic cells vary significantly, depending on the morphology of fullerene phase: whether it is bulk phase (as in the case of bi-layer structures) or nanocrystals (as in the case of the polymer-fullerene blends).

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